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1. Project	A fundamental study of the chemical and physical changes taking place in the rapid tannage of heavy leather to obtain information pertinent to the development of new rapid tanning processes.
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1. SUMMARY

The increased use of substitute materials has caused serious concern, particularly to the heavy leather industry. For example, previous to the introduction of synthetics, hides used to be imported into U.S. to meet the demands of this industry but the situation has been reversed now and the U.S. Livestock Industry must seek foreign outlets for 6-7 million surplus hides every year.

Leather is still acknowledged to be superior to synthetics, but its comparatively high cost is detrimental to its own interests. Hence, bringing down the cost of production is very important and herein lies the need for quicker methods of heavy leather tannage.

During the present investigation, work on fundamental lines was carried out initially to determine the optimum conditions for rapid tanning like pretreatment of the pelt and control of, temperature, concentration, pH etc., of the tan liquors. Studies were also carried out on the fundamental and practical aspects of some of the pretanning operations like normal and short liming, deliming, pickling, depickling, etc. The influence of swelling of the pelt on the penetration and fixation of tannins, was studied in detail. These studies paved the way for successful tanning experiments in the laboratory, which were later translated on a pilot-scale in the tannery.

As a result of the above, two simple methods of rapid tanning have been developed. According to these methods, sole leather with properties, consistent with the normal specifications could be tanned in less than three weeks. The methods are extremely easy and economical and ideally suited to the conditions prevailing in India. Also a new way of vegetable tanning which could be successfully employed for heavy leather tanning in general, including bag tanning in the village sector has been developed. In addition, certain allied problems, usually encountered in heavy leather tanning,

like leaching of vegetable tanning materials, better utilisation of tanning materials available locally, were tackled and resolved successfully.

On a more fundamental level, studies on the viscosity of tan liquors, the rate of penetration of different tan liquors through gelatin column and pelt pieces, layerwise study of tanned pelt, chromatographic studies of tannin infusions, etc., were carried out and the results have been incorporated in the respective chapters.

2. INTRODUCTION

2.1 Importance of the problem - Threat from synthetics

Although the increased use of substitute materials has caused serious concern to all the segments of the tanning industry, the heavy leather branch has been affected most severely. Heavy leather is used where thickness, firmness, and solidity are needed, as in shoe soles, luggage, upholstery and industrial belting. Until the successful introduction of synthetics began some twenty years ago, the entire U.S. production of heavy hides and a sizable quantity of imported hides, were required to meet the demands of this industry. To-day the situation has been reversed. Because of the encroachment of synthetic materials into leather markets, the U.S. Livestock Industry must seek foreign outlets for 6-7 millions surplus hides each year.

Leather is still acknowledged to be superior to the man-made materials in most of the essential respects, and undoubtedly will continue to benefit from its established 'prestige' factor. The real threat to the industry lies in the comparatively high cost of leather. To retain its position in a competitive market, the leather industry is realizing the need for special and determined efforts in the direction of processing economics.

Tanning of heavy leather used to take a very long time in the past and even now, 2-3 months are needed in certain tanneries, to turn out a finished product. But unless the underlying principles are fully understood and the processes can be controlled, attempts at accelerating the rate of tannage under arbitrary conditions may affect the quality and performance of the leathers produced.

A sole leather should be strong and reasonably tough and should possess good abrasion resistance and

low water absorption. A good colour is also desirable since it appeals to the selective taste of the buyer. Apart from these, on the point of chemical analysis, the leather should have a high degree of tannage and low water soluble content. From the commercial point of view, the yield is also very important. Hence, any attempt at rapid tanning should take into consideration all the above aspects.

2.2 History of rapid tanning

Attempts at rapid tanning dates back to the year 1927, when Pawlowitsch[1] started pioneering work in this direction. He studied the rate of penetration of tannins through the pelt, at different pH levels and temperature. Later, Belavsky and Fiksl[2] stressed on the proper co-ordination of concentration, temperature and pH of tan liquors. The increase in the strength of liquors brings about peptisation and aggregation of the tannin particles, incidental to relatively high concentrations. Rise in temperature as well as decrease in acidity, increase the degree of dispersion of the tannin molecules facilitating penetration. Increase[3] in pH also lessens the affinity of the tannin for the pelt. Therefore, rapid colouring of the pelt is facilitated at higher pH while an increase in acidity assists the combination of tannin and pelt.

In 1943, Humphreys[3] suggested a three pit strong liquor tannage and since then many methods of rapid tannage have been evolved. But the major drawback in many of these methods, is that the tail liquor is not easily exhausted.

Recently Atkinson and Cutting[4] devised a simple rapid tannage. Fully delimed hides are first tanned in pits containing Mimosa liquor at 15°Bk and then they are drum tanned in concentrated liquor for 36 hours. The liquor left behind in the drum is withdrawn and diluted to 15°Bk for use in the pits.

Similar investigations were made by Humphreys and

Chand[5]. They developed a simple two pit system of rapid tanning, eliminating the use of a drum. This process is an easy one and can be adopted by any village tanner.

Giving his impressions about the recent developments in sole leather, Herfeld[6] commented about the adverse effect of 'closed' tanning system, by which the tanning agents are quantitatively absorbed by the hide. Because of the prolonged drumming without float as required by one of the methods, the firmness properties of the leather are considerably lowered. Long drumming would inevitably result in an undesired change in the fibre structure. For this reason, he preferred the 'open tanning systems' and a limited tanning time of one to two weeks. Also these procedures can be regulated in an exact manner and lend themselves to fully automatic control.

2.3 Factors involved in rapid tanning

Herfeld mentioned the following factors, which are important for rapid tanning in general.

(1) The tannin must be brought into the hide in such a way that first of all, the tanning material must penetrate into every fibre and every fibril. Subsequently the fibres and fibrils may be covered with tanning materials.

(2) The sapping of the tan liquors is accomplished by the application of the countercurrent principle by which the coarsely dispersed particles are in preference taken out of the polydispersed system through a selective absorption of the tannins.

(3) The liquor concentration must be increased in a short time. Premature tanning fixation should be prevented by suitable control. Proper pH adjustment should also be made.

Use of large quantities of salt should be absolutely avoided. Sweetened extracts, syntans and

lignosulfonates should contain as little salt as possible.

(5) By raising the temperature, a better solubility and a reduction in particle size are obtained. Thereby the tanning process is speeded up, the problem of sludge formation is reduced, the tanning agents are better utilized and the leather yield is increased. In this way, not only the tannage itself is accelerated but we obtain also a considerably deeper penetration of the tannage due to the reduced particle size. Temperatures upto 100°F can be used.

(6) The pelt should be completely delimed and must undergo a pretannage which ought to fix the right degree of fibre swelling until the main tannage takes hold. Anionic pretannage is preferred.

In giving certain interpretations regarding the tanning velocity in the rapid tanning of leathers, Woollenberg[7], has mentioned that the tanning time was reduced by a factor of 2.6 by raising the temperature from 8° - 18°C and by a factor of 2 by increasing the strength of the liquor from 80-140°Bk. He has suggested, for rapid tanning, the use of a suitable tanning mixture of low viscosity as well as a drum in the intermediate stage maintaining the liquors at as high a temperature as permissible.

2.4 Recent popular methods

Two processes have been recently developed in South Africa viz., osmotan process and the Liritan[8] no effluent process. The former avoids the usual deliming, the unhaired hides are pickled in 1.5 per cent H_2SO_4 and 10 per cent NaCl for a day and then kept in tan liquor (25°Bk) at pH 3.0. Deliming is completed during surface tanning. Then the hides pass through four tan pits with the tan liquor varying from 61° to 84°Bk while the pH rises from 3.1 to 3.3. The hides remain for one day in each pit and the counter current system is followed.

In the Liritan process, the hides are limed for 3 days and pickled with salt, acid and 2 per cent calgon. Surface tanning is done in a pit with 20°Bk liquor at pH 3. The hides are then entered into strong liquors (67-100°Bk). They are finally drummed with powdered wattle extract and fillers.

Various methods of pretreatment have been suggested from time to time by the research workers engaged in the problem of rapid tanning. Chrome, chrome or aluminium complexes with syntans, dialdehyde starch[9], alkali metal nitrites, syntans, formaldehyde, calgon, polysaccharide bisulfites, etc., are some of the pretanning agents developed successfully for rapid tanning.

Coming to some of the modern methods, Humphreys[10] suggested a rapid sole leather tannage with a sulfited wattle liquor, dispensing with any form of separate deliming. Wattle liquor containing 10-12 per cent of $NaHSO_3$ on the weight of the extract, is brought to 70°Bk and pH 3.0/3.2 (with HCOOH). Limed pelt is then entered into the liquor. Almost complete penetration is obtained in 2-3 days.

Rapid Mimosa tannage with simultaneous deliming has been mentioned by Atkinson and Cutting[11] also, during the same period.

A rapid method of theoretical interest has been developed by Schnoller[12]. The process consists of partially tanning the hides with a non-vegetable tanning agent followed by mechanically expressing out the excess water (to about 30 per cent reduction in weight) and then tanning with a vegetable tanning extract, till the tannin uptake is roughly equal to the weight of water expressed out earlier.

Some of the methods developed in Russia merit considerable attention in the context of Rapid Tanning. Mihailov and Suchkov[13] developed a quick process where steer hides were pit soaked, for 48 hours, pit limed for 2 days, pickled without deliming, and treated with

0.5 per cent Cr_2O_3 at 45-48 per cent basicity. Vegetable tanning was done with 30 per cent tannins on limed weight. Final temperatures of 50°C to 55°C were used. In certain other instances, there have been attempts to precondition the pelt to the required pH by treatment with buffers, prior to vegetable tanning. It has been conclusively shown that the pelt which has been brought to the isoelectric point[14] can be tanned straight in pits with warm strong tanning liquors. The tanning takes place without shrinkage or hydrolysis. Cronin[15] of Rohm and Haas, has developed a process in the above pattern.

2.5 Quickening of beamhouse operations

Simultaneous with the rapid tanning, efforts have been made to shorten the period of pretanning operations. Drum liming has been attempted by several workers. Herfeld[16] and Van Vlimmeren[17] suggested one day's drum liming as against 6 or 7 days pit liming. In Russia, Leonov[18] developed a process for accelerated soaking and liming of heavy hides. The hides are drum washed 30 minutes in the cold, then 30 minutes in warm water, head split and fleshed. They are again soaked in water containing 5 per cent Na_2SO_3. After 3 hrs, 2 per cent on pelt weight of orizon (Aspergillus oryzae enzyme) is added. The hides are drummed for less than 8 hrs, washed and limed in the same drum with 1.5 per cent Cao and 0.06-0.07 per cent Na_2S (wt/volume). The drum is run for about 6 hrs.

Rapid oxidative unhairing methods are becoming more and more prominent of late. Rosenbusch[19] and Teplenzky[20] and Glenz have made definite contribution in this field. According to the latter, work trials on rapid unhairing with Imprapell Co., have shown that the resultant leather fully meets the quality requirements of the footwear industry. The time can be curtailed by an intermediate treatment with alkali, which loosens epidermis and hair in just

three hours. Also this method reduces the consumption of water and consequently the effluent disposal is made easier.

2.6 Plan of approach adopted in the present investigation.

In our study of rapid tanning extending through the tenure of the scheme for the last five years, we have first studied the varied aspects of fundamental nature related to rapid tanning and then translated the findings on pilot plant scale to be further utilised on industrial scale. Also we have studied alongside, allied problems like the extraction of vegetable tannins, blending of tan materials, sludge formation in the tan yard, etc. The results are presented in this report under the respective chapters.

3. DIFFERENT EXPERIMENTS IN RAPID TANNING

3.1 Effect of swelling on heavy leather tannage

The phenomena of swelling and plumping have great significance in the manufacture of heavy leathers. Swelling tends to make the reactive groups of protein accessible to the tannins, by widening the intermolecular spaces and above all by the rupture of crosslinks, particularly H bonds due to the contraction of protein chains and widening of the gap between adjacent collagen chains in certain regions. This influence of swelling tends to increase the fixation of tans. In sole leather, where compactness, high wear resistance and a good yield are important, it is customary to allow the pelt to acquire the desired swelling during liming by means of suitable addition of alkali.

Marriott[21] while studying the swelling of collagen found that the acid swelling commenced from pH 3.5 downwards, and alkaline swelling from pH 9.5 upwards. The swelling is minimum at pHs near the

iso-electric region of the pelt.

3.1.1 In the present study, it was attempted to study the extent of swelling of delimed pelt at different pHs and the effect of such swelling on the speed of penetration and the extent of fixation of vegetable tannins.

Experimental

A wet salted buffalo hide (heavy) was soaked and limed as for sole leather manufacture. After unhairing, fleshing and washing, small pieces of dimensions 2.5 inches x 2.5 inches (weighing nearly 30 gms.) were cut off from the butt portion of the hide. The pieces were then completely delimed with boric acid and washed well in repeated changes of distilled water.

Using the buffer system of sodium acetate and hydrochloric acid (50 cc N-CH_3COONA + N HCl in required quantity) buffer solutions of pHs varying from 2.5 - 5.8 were prepared. Delimed pelt pieces were wiped free of surface water, pressed between folds of filter paper and then weighed and their thicknesses measured as nearly as possible by means of a gauge. Then the pieces were put in the buffer solutions of different pHs prepared as above and they were allowed to remain there for 48 hrs. The float was about 400 per cent on the weight of the pelt piece. During this period the pH was maintained at the respective levels by the addition of required amounts of dil. HCl. After 48 hrs., when the system had attained equilibrium the pieces were taken out, pressed between folds of filter papers and weighed. Their thicknesses were also measured. The findings are tabulated in the next page.

Table No.1

No.	pH	Average thickness Initial mm	Average thickness final mm	Grams weight initial	Grams weight final
1	2.5	6.2	8.4	26.4	29.5
2	3.0	5.2	7.0	26.4	29.6
3	3.5	5.2	6.4	26.5	30.0
4	4.0	5.1	5.7	23.3	26.8
5	4.5	5.1	5.7	24.1	23.4
6	4.8	6.5	6.1	36.3	36.0
7	5.3	5.2	4.9	24.8	24.0
8	5.8	5.4	5.3	25.3	24.1
9 control	6.0	5.8	--	23.0	--

It may be observed from the above table that there is increase in weight and thickness in the lower pH ranges (2.5 - 4) while at increasing pHs especially near the I.E.P. there appears to be a slight depletion and loss in weight.

Now the pieces were taken straight for vegetable tanning. No washing was given since it was felt that it would alter the pH and physical condition of the pelt pieces. The pieces were placed in wattle liquor of 25°Bk and the strength was raised to 50°Bk after three days. The total tannins given corresponded to about 30 per cent on pelt weight. A total tanning time of 10 days was given in all the cases. The pieces were observed for penetration each day till completion. The observations are recorded in the table given in the next page.

Table No.2

No.	pH	Penetration 2nd day	3rd day	4th day	5th day	6th day	7th day	8th day	9th day
1	2.5	Negligible	traces	1/3	1/3	1/2	3/4	Full	--
2	3.0	-do-	-do-	1/3	1/3	1/2	3/4	Full	--
3	3.5	a little	1/3	1/2	3/4	3/4	Full	--	--
4	4.0	nearly 1/3	1/3	1/2	3/4	90 per cent	Full	--	--
5	4.5	-do-	-do-	1/2	3/4	-do-	-do-	--	--
6	4.8	-do-	-do-	-do-	-do-	Full	-do-	--	--
7	5.3	-do-	-do-	-do-	-do-	Full	--	--	--
8	5.8	-do-	-do-	-do-	-do-	90 per cent	Full	--	--
9 control	6.0	-do-	-do-	-do-	-do-	-do-	Full	--	--

From the data it may be observed that the penetration is very much retarded at the lower pHs, of 2.5 and 3.0. Between pH 3.5 and 4.5 the penetration rate is better but it is lower than that of the control. Near the iso-electric point region of the pelt, we find that the penetration is fairly rapid and slightly quicker than that of the control.

The tanned pieces were washed, very lightly oiled and allowed to dry. Then they were weighed to assess their yield and their thickness were also measured. Also their general physical characteristics were comparatively assessed.

Table No.3

No.	pH	Colour	Feel	Thick-ness mm	Per cent yield
1	2.5	Dark	Hard and tough	8.0	71.6
2	3.0	Dark	-do-	8.0	71.4
3	3.5	Lighter than 1 but darker than control	Less hard	7.2	71.3
4	4.0	Lighter than 3	Less hard than 3	6.6	67.5
5	4.5	Good colour better than control	Feel same as control	7.0	71.0
6	4.8	-do-	-do-	7.1	68.5
7	5.3	-do-	Softer than control	6.7	67.0
8	5.8	Same as control	Same as control	7.0	57.0
9	con-trol	--	--	6.6	59.0

From the above data it may be seen that in the case of pHs 4.5 and 4.8, the tanned pieces possess good colour, desirable feel and reasonably good yield. Pre-conditioning the pelt below 3.5 i.e. allowing the pelt to swell to its maximum does not seem to be desirable, since apart from the very slow penetration, the final leather is excessively hard and its colour is also dark. Higher pHs (above 5.3) tend to soften the leather and the yield also suffers in comparison.

The pieces were analysed to find the degree of tannage and the results are reported in Table 4.

Table No.4

No.	pH	Moisture	W.S.	Hide substance	Fixed tans	Degree of tannage.
1	2.5	13.62	7.36	47.37	31.65	66.8
2	3.0	15.25	10.14	40.06	34.55	86.2
3	3.5	13.50	10.01	43.05	33.45	77.7
4	4.0	15.0	9.80	42.66	32.54	76.3
5	4.5	14.50	11.00	42.28	32.22	76.2
6	4.8	14.0	10.50	43.30	32.20	74.3
7	5.3	14.20	11.20	43.00	31.60	73.5
8	5.8	14.10	12.00	43.50	30.40	69.90
9	control	14.95	9.68	47.57	27.80	59.0

(Oil content and insoluble ash negligible)

From the data, it may be observed that the fixation is maximum in the case of pH 3 and there is decreased fixation at higher pHs. Also it may be seen that near the iso-electric region of the pelt, the tan fixation is quite good and since at this pH range, the penetration is also quick and the properties of the tanned leather are better than those of the control, it is felt that it is advisable to precondition the pelt to its i.e.p. while aiming at rapid tanning.

3.1.2 In continuation of the above work, it was attempted to fix the swelling with some suitable reagent like HCHO, before the actual commencement of the tanning to obviate the possibility of sudden depletion or deplumping as soon as the pelt came into contact with the tan liquor. According to Gustavson, one of the main practical applications of HCHO is for the fixation of swelling of the grain in order to maintain the desired degree of swelling. Then the stabilised hide can be tanned in rather strong solutions of vegetable tanning extracts, with considerable saving

of time, without case hardening or impaired quality of leather.

In our experiments, pelt pieces were allowed to swell in various solutions of adjusted pH differing between 2.5 and 5.8. After measuring the extent of swelling after 48 hours of treatment, when the system had attained equilibrium, the pelt pieces were treated with a one per cent solution of HCHO for about 2 hours in order to set the swelling. Measurements were taken after this treatment. But it was found that the swelling had not been really fixed and there were changes in the degree of swelling and that too especially in the lower pH values. Here the swelling increased still further. At pH values between 3.5 and 4.8 also, there was increase in swelling to a small extent.

During the course of the subsequent vegetable tanning, it was observed that though there was no case hardening in any of the pieces, the penetration was extremely slow at the lower pH values. As expected, the penetration under the isoelectric regions was rapid.

Continuing the work on swelling it was attempted to study the effect of neutral and alkaline swelling of the pelt on the subsequent tannage. Delimed pelt pieces were treated with buffer solutions of pH values varying between 6-11 and subsequently they were vegetable tanned. It was found that the rate of penetration was going down with increasing pH values of the pretreated pelts. So also, the colour of the tanned piece as well as the yield deteriorated in the higher pH values.

3.2 Pretanning/preconditioning etc. of the pelt

Of the several approaches made to arrive at rapid tanning techniques, one of the foremost and earliest was the attempt to pretreat or condition the pelt suitably before the actual vegetable tanning. Several

pretanning agents like chrome, chrome or aluminium complexes with syntans, formaldehyde, calgon, polyoxysaccharide, bisulfites, have been used in the past. In certain other instances, there have been attempts to precondition the pelt to the required pH by treatment with buffers prior to vegetable tanning. It has been conclusively shown that pelt brought to the isoelectric point can be tanned straight in pits with strong warm tanning liquors. The tanning takes place without any shrinkage or hydrolysis, a heavy hide needing about one week to get struck through and two weeks to get the maximum yield.

In our experiments, the following preconditioning/pretanning systems were tried.

I. Conditioning the pelt before tanning by buffer treatment or otherwise to a pH of 4.8

(a) Sodium acetate + acetic acid
(b) Sodium citrate + citric acid
(c) boric acid + dil.HCl
(d) Formaldehyde + formic acid

II. (a) Pickling - HCl + NaCl
(b) Pickling - H_2SO_4 + NaCl for Osmotan process

III. Formaldehyde pretreatment

IV. Chrome pretreatment

V. Tanning at elevated temperatures

VI. 'Straight through' tanning of limed pelt in a modified wattle liquor

VII. Control

Experimental

One wet salted buffalo hide was soaked and limed according to the usual procedure for sole leather manufacture. After unhairing, fleshing and washing, pieces of dimensions 8 inches x 8 inches were cut off from the butt portion. These pieces were taken for the tanning experiments after noting down the weight of each piece.

For the first set of experiments the pieces were completely delimed with boric acid, washed well and then left in the respective buffer solutions for 48 hours to attain equilibrium. 0.1 molar solutions of the buffers were used and a uniform float of 400 per cent on pelt weight was given for each piece. A few drops of thymol dissolved in acetone were added to prevent any putrefaction.

The pH was maintained at 4.8 by occasionally adding citric acid or acetic acid.

I(c) The pelt was delimed with boric acid and then left in 1 per cent boric acid solution (float 400 per cent). Dilute hydrochloric acid was added occasionally to maintain the pH at 4.8 and the pelt was left for about 48 hours.

I(d) In the case of HCHO treatment, 1 per cent HCHO was used with a 400 per cent float and the pH adjusted to 4.8 with formic acid.

II(a) Limed pelt was pickled with 5 per cent NaCl and dilute hydrochloric acid was added in small amounts. The pelt was frequently handled till pH was approximately 4.8.(b) Limed pelt was pickled with NaCl and H_2SO_4 as in Osmotan process.

III.Delimed pelt was pretreated with 1 per cent HCHO in 400 per cent float for 48 hours.

IV.For chrome pretreatment, the pelt was delimed and pickled with 1.25 per cent H_2SO_4 and 6 per cent NaCl. It was then chrome-tanned using a liquor with 0.6 per cent Cr_2O_3 content (on pelt weight) and 48 per cent basicity. Penetration was found completed in 36 hours, vegetable tanning was then commenced.

V.For tanning at higher temperature, pelt was completely delimed with boric acid, washed and then kept in 50°Bk wattle liquor (35-40°C). After 24 hours, the temperature was raised to 40-50°C. The strength of liquor was raised to 70°Bk after 3 days and the

temperature maintained at 45°C for the rest of the tanning period.

VI. Modified bisulphited wattle liquor was prepared using 1 part wattle extract, 1 part water and 10-12 per cent sodium bisulphite. Then HCOOH was added to bring down the pH to 3.0 - 3.2 and the liquor was diluted to 70°Bk. Limed pelt was kept straight in this liquor.

VII. For the control, pelt was delimed completely with boric acid and then vegetable tanned.

All these pretanning/preconditioning operations were carried out in glass troughs (25 cm. diameter) under laboratory conditions. The subsequent tannages were carried out in the same troughs after draining the liquors.

Vegetable tanning

In the Osmotan process, the pickled pelt was placed in 25°Bk wattle liquor at pH 3.0 for 24 hours before its transfer to 60°Bk liquor. The pelt was then successively tanned in 67°, 74° and 80°Bk liquors at intervals of one day using the counter current principle. Four hundred per cent float (on pelt weight) was employed in all the cases. The tanning was completed in only five days.

For the control, the delimed pelt was first placed in 25°Bk liquor for 24 hours. The strength was raised to 50°Bk and after three days, to 70°Bk.

The tannages for tanning at higher temperature and 'tanning of limed pelt with bisulphited liquor' were done as described earlier.

The buffer treated pieces were kept straight in 50°Bk wattle liquor and tanned for 3 days, the strength of liquor was raised to 70°Bk and the tannage completed.

The pH of wattle liquor was adjusted to appropriate levels in Osmotan process and in the experiment with bisulphited wattle liquor. In all other cases, wattle liquor at its natural pH was used throughout.

Table No.5. Rate of penetration, colour, feel and yield of leathers

Treatment	Penetration time (days)	Colour	Feel	Yield (per cent)
I.(a) (i) NaAc + HAc	6		Same as control	64
(ii) NaCi + HCi	6		-do-	64
(b) Boric acid	7		-do-	63
(c) HCHO	7	Same as control	Slightly tougher	61
II.(a) NaCl + HCl	6	Better than control	Same as control	59
(b) Osmotan process	4	Darker than control	Tougher	67
III.HCHO pretreatment	7	Same as control		56
IV.Chrome pretreatment	7	Darker than control	Tougher	65
V.Tanning at higher temperature	3½		Little spongy	55
VI.Limed pelt	6	Very good	Softer	56
VII.Control	9	Good	Softer	56

Table No.6 Chemical analysis of leathers

	Moisture (per cent)	Oils and fats (per cent)	Water solubles (per cent)	Total ash (per cent)	Insoluble ash (per cent)	Hide substances (per cent)	Degree of tannage
I.(a) (i) NaAc + HAc	15.5	0.50	7.8	0.45	0.20	42.94	76.7
(ii) NaCi + HCi	14.5	0.40	10.4	0.50	0.24	42.34	75.8
(b) Boric acid	14.2	0.61	10.4	0.60	0.25	45.68	70.46
(c) HCHO	14.5	0.50	4.0	0.55	0.23	43.00	87.0
II.(a) NaCl + HCl	13.5	0.46	5.0	0.60	0.26	45.00	77.4
(b) Osmotan process	14.1	0.60	7.5	0.62	0.30	41.50	86.70
III.HCHO pretreatment	13.3	0.41	4.2	0.56	0.30	49.90	63.5
IV.Chrome pretreatment	15.0	0.58	4.0	1.50	1.24	48.50	59.8
V.Tanning at higher temperature	14.6	0.60	9.3	0.42	0.30	47.00	60.0
VI.Limed pelt	13.4	0.52	10.48	0.58	0.24	45.55	65.4
VII.Control	13.7	0.50	4.5	0.48	0.25	51.75	56.3

In experiments except Osmotan process, the duration of tanning was 12 days and the total amount of tannins given was about 30 per cent (on pelt weight). In Osmotan process, the amount of tannins could not be calculated since the counter current method was adopted.

After the completion of the tanning, the pieces were washed, lightly scrubbed on the surface, very lightly oiled and allowed to dry. No bleaching or myrobing was given.

During tannage, the time taken for complete penetration in each case was noted. The tanned pieces were also assessed for their feel, colour and yield. The leathers were analysed for important physico-chemical properties like degree of tannage, abrasion resistance and water absorption. The results are presented in Tables, 5,6 and 7.

Discussion

From the Tables it may be observed that the time required for complete penetration is shortened in all the pretanning/preconditioning systems, compared to the control. Adjustment of pH of the pelt to 4.8 (i.e.p.) either by use of buffer salts or by boric acid and hydrochloric acid, prior to tanning, facilitated quicker penetration which was completed in 6-7 days as against 9 days (control).

Rise in temperature of tan liquor leads to rapid penetration and the pelt is struck through in 90 hours. But prolonged treatment in hot liquor impairs the structure of the pelt. The tanned piece was a little spongy and its chemical and physical characteristics were not comparable to those of the control.

Osmotan process resulted in rapid penetration, in the case of limed pelt tanned straight in modified wattle liquor, penetration was completed in less than six days. Osmotan process gave the highest

yield (67 per cent) followed by chrome retan process (65 per cent). In the tannages with buffer treatments, the yield varied between 61 per cent and 64 per cent, tanning at higher temperature and straight tanning of limed pelt gave comparatively low yields. The buffer treated leathers gave almost the same feel and colour but better compactness than those of the control. Limed pelt tanned straight with modified wattle liquor gave leathers with very good colour but with less fullness and softer feel. Formaldehyde treated leather was fuller and tougher than that of the control. Osmotan, chrome pretreatment and tanning at higher temperatures gave darker leathers, in the former two, leathers were tougher.

Table 6 shows that HCHO pretreatment and the Osmotan process give high degree of tannage. The buffer treated samples have good tannin fixation, the degree of tannage ranging from 70-76 per cent. But these leathers possess comparatively higher water solubles content (7.8 - 10.4 per cent). In the other experiments, the degree of tannage is about 60 per cent as compared to 56.3 per cent in the control.

Except in Osmotan and chrome pretreatment processes, there is less abrasion resistance and more water absorption in all other cases as compared to the Control (Table 7). In the case of Osmotan, the physical properties are slightly improved while in chrome pretreatment, the properties are almost the same as those of the control. In other pretanning/preconditioning systems, penetration is quicker and fixation greater, but some of the physical properties are not comparable to those of the control. As one of the most rapid tanning processes, Osmotan process alone imparts the required physical characteristics of normal sole leather, despite its disadvantages like lack of simplicity and need for adequate control.

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	Abrasion resistance Loss of thickness(mm)		Water absorption(per cent)		T_s
	100 revns.	500 revns	2 Hr.	24 Hr.	
I.(a) (i) $Na\overline{Ac}$ + $H\overline{Ac}$	1.79	4.44	60.8	67.3	87
(ii) $Na\overline{Cl}$ + $H\overline{Cl}$	2.05	4.69	64.1	70.1	87
(b) Boric acid	2.38	5.00	65.2	70.1	86
(c) HCHO	1.81	4.62	62.2	67.8	88
II.(a) NaCl + HCl	1.96	4.52	66.1	72.9	86
(b) Osmotan process	1.73	3.40	54.0	58.1	88
III.HCHO pretreatment	2.24	5.00	61.3	65.2	85
IV.Chrome pretreatment	1.93	4.05	56.1	58.5	89
V.Tanning at higher temperature	1.91	4.55	62.0	67.1	82
VI.Limed pelt	1.93	4.75	68.3	72.4	86
VII.Control	1.96	3.89	55.2	59.2	85

Subsequently the work was repeated using Babul liquor since the above material is very much used in most of the regions of India for sole leather tannage. The process was slightly altered as follows.

Babul liquor of 50°Bk was used to start the tanning, except for the control, where a liquor strength (25°Bk) was used initially. After 3 days, the concentrations were correspondingly raised and the tannage was completed at 70°Bk, in all the cases except for the Osmotan process where the final Bk was adjusted to 80°Bk. The extent of penetration was noted every day for each experiment and the findings were recorded.

General findings

During the course of the tannage, the following broad observations could be made.

(1) A slight precipitation was observed in the case of formaldehyde pretreatment, probably due to the interaction of babul tannins with formaldehyde.

(2) In the Osmotan process where the pH of the liquor was lowered to 3.0 - 3.2, no precipitation was observed, while in the case of wattle tannage, there was a tendency for precipitation at this low pH.

(3) Regarding the rate of penetration and the rapidity of the tannage as a whole, practically the same trend as in the case of wattle tannage was observed here also. Osmotan gave the quickest tannage and the rate of penetration decreased in the following order.

Osmotan - Limed pelt, tanned in sulfited liquor - tanning at higher temperature - buffer treatment at pH 4.8 - chrome pretreatment - HCHO pretreatment at pH 4.8 - HCHO pretreatment at normal pH - Control.

The pieces after tanning were washed, very lightly oiled and allowed to dry. Then they were weighed to arrive at their yield and also their physical characteristics were assessed. The results are tabulated in the Table given in the next page.

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Control	9 days	Slightly reddish tinge	Good temper	53

Discussion

From the results it may be observed that Osmotan process and the buffer pretreatment process gave good results by way of rapid penetration, good fixation and desirable physical properties. For hard and firm soles, Osmotan process seems to be ideal while for flexible soles and repairers bends the buffer pretreatment may be quite suitable. Buffer treatment with sodium citrate and citric acid imparts a very light colour to the leather and this has been confirmed by larger tanning trials in the tannery.

Tanning of limed pelt straight with bisulfited babul liquor is a simple and quick process but the resultant leather lacks the required fullness and temper. The yield is also comparatively low.

Regarding the buffer pretreatment with sodium citrate and citric acid, it may seem that the cost involved is considerable, since both these chemicals are known to be costly. Hence particular mention is made here that subsequent tanning trials on a bigger scale have shown that the buffer solution once prepared can be re-used for several successive lots (9-10 lots) provided that the concentration of the buffer is maintained by proper replenishment of the acid and salt and a suitable bactericide like thymol is used in the buffer to prevent any possible bacterial deterioration. It has been found by analysis, that the actual quantities of citric acid and sodium citrate consumed by each lot of delimed pelt passing through the buffer solution are very little. The costing for the buffer pretreatment for a number of lots has been worked out in detail and it has been found that it works out to only a few paise per pound of delimed pelt. But the advantages that can be derived from this process are commensurately high since the process cuts down production time and also ensures good yield and a pleasing light colour. Especially with tanning materials like mangroves which impart a very dark colour to the leather, this process is highly beneficial.

3.3 Use of dialdehyde starch

Among the various pretanning agents employed for the rapid tannage of sole leather, dialdehyde starch has attracted considerable attention after the pioneering work of C.W.Beebe (U.S.Patent) and further work by Wagoner[9], Windus, et al. The latter workers found out that satisfactory pretanning could be obtained with 5 per cent DAS on pelt weight and that the solution could be re-used at least 9 times by

re-strengthening with 3 per cent DAS. A stock solution of DAS (25 per cent) dissolved with borax and having a pH of approximately 5 is stable for at least one month.

In our experiments, a few pieces of delimed buffalo hide were pretanned with DAS. Completely delimed pelt pieces were placed in DAS (5 per cent on pelt weight) which was dissolved in borax and kept at a pH of 8, for 48 hours. After this pretanning, the pieces were placed in a 50^{o}Bk wattle liquor for 3 days. Subsequently the strength was raised to 70^{o}Bk.

It was found that the penetration of vegetable tannins was over in six days. The leathers produced were quite full and compact. The general physical and chemical properties were good, as a whole.

This is an easy and quick process. But in India there is no regular production of this material and hence this has to be imported which will raise the cost of production at the Indian Market level. Further, a little difficulty was experienced in dissolving this product.

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In our experiments on the above lines, extra thick buffalo hide pieces from the butt portion was chosen and they were placed in 3 per cent sodium nitrite solution for about 2 hrs. Then dilute formic acid was added and the pH was adjusted to 4.5 - 6. The pelt was left in the bath for 24 hrs. The pH was adjusted to about 5 with formic acid during this interval. Then the solution was drained out and

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wattle liquor of 50°Bk was employed for tanning. After one day the Bk was raised to 80° and it was found that the pelt was completely penetrated in less than 90 hrs.

This was found to be a very quick method of tanning.

As a variation of this process, one experiment on rapid tanning was tried using sodium sulphite instead of sodium nitrite. Here, with the addition of weak acid to adjust the pH, sulphurous acid was produced in solution instead of nitrous acid. On subsequent vegetable tanning, with wattle liquor (50°Bk) penetration was found to be over in 5 days. Also, it was found that the tanned piece had a very light colour, presumably due to the bleaching action of SO_2.

3.5. 'Dry' tanning experiment

Certain 'dry tanning' experiments were conducted for the rapid tanning of sole leather. The process are briefly described as follows:-

3.5.1. Process I

Raw material — Wet salted buffalo hide

(1) Soaking for 4 hours in three changes of water

(2) Liming - 3 days

Slaked lime: 6 per cent

Sodium sulphide: 1 per cent

Float: 400 per cent { ½ vol. once used lime liquor
{ ½ vol. fresh water

(3) Unhairing and reliming (3 days)

Lime: 6 per cent

Caustic soda: 0.5 per cent

Water: 400 per cent

(4) Fleshed and noted the fleshed weight.

(5) Completely delimed with 3 per cent ammonium sulphate and 100 per cent water.

(6) Pickling

Salt:	5 per cent
Sulphuric acid:	0.5 per cent
Water:	100 per cent

(7) Pretreatment

Sodium bisulphite:	5 per cent
Water:	100 per cent

pH adjusted to 4.6 with formic acid and drummed for one hour.

(8) Tanning:

(1) Put in 50°Bk liquor for 3 days

(2) Changed into 80°Bk liquor for 3 days.

Then one side (A) is put in the same liquor for one more day. The other side (B) is powder tanned with 15 per cent wattle extract powder for 7 hours. Then it is just dipped in a 80°Bk liquor to remove the adhering extract on the surface of the leather.

Both sides (A and B) piled for one day.

Next day both sides were washed and bleached with 1 per cent Syntan NC and 1/4 per cent oxalic acid, washed, beamed and put in 30°Bk liquor for one day.

Next day stuffed with

Raw Pungam Oil:	3 per cent
Glucose:	2 per cent
Epsom salt:	1 per cent

in a drum, taken out, set and finished.

(A) Leather yield without powder tanning: 52.8 per cent

(B) Leather yield with powder tanning: 52.2 per cent

Remarks

There was not much advantage in giving powder drum tannage after liquor tanning. The same leather yield would have been obtained even by drumming in 90 - 95°Bk for 6-7 hours.

Another disadvantage is that the extract powder

is smeared on the side of the leather and most of it remains outside, with only a small quantity penetrating into the leather.

3.5.2 PROCESS II

Drum deliming without float and then powder tanning

(1) Soaking and liming as in Process I.

(2) Deliming without float

Naphthalene sulphonic acid:	4 per cent on fleshed wt.
Glacial acetic acid:	0.75 per cent dissolved in 3 times of its weight of water

Drum run for 3 hours and tested pH of the pelt which should be between 5 - 5.2.

(3) Pretanning:

C.L.R.I. Syntan NB - 8 per cent, drum run without float for 1½ hours pH of the pelt 4 - 4.5

(4) Powder tanning

The pretanned pelts are drummed with 25 per cent spray dried wattle extract powder for 3 hours.

Then 20 per cent more of spray dried wattle extract is added and drummed for 35 hours.

Tanning is completed and the sides are piled for one day.

(5) Bleaching:

C.L.R.I. syntan N.C.:	1 per cent
Oxalic acid:	1/4 per cent

The leathers are washed and myrobed for one day

(6) Stuffing:

T.R.O.:	1.25 per cent
Raw pungam oil:	1.25 per cent
Epsom salt:	1 per cent
Glucose:	2 per cent

Drum run for one hour. Taken out, conditioned, set, dried and rolled.

Observations

Even though the tanning could be completed in a very short time, the bellies and shoulders showed pebbling. Even after heavy setting the creases were prominently visible.

Hence complete powder tanning on whole buff hides is not very practicable. But if the bellies and shoulders are tanned separately in liquor, the butts can be tanned by this rapid process.

3.6 A simple rapid tannage for sole leather

Most of the methods suggested hitherto for rapid tanning suffer from the following disadvantages as far as the conditions in India are concerned.

(a) The tanning material used is mostly wattle or a blend of imported extracts like quebracho, chestnut, etc. The acid used to bring down the pH is usually formic acid which is also fairly costly.

(b) The principal raw material in India are buffalo hides, which are loose in structure as compared to the compact ox hides used in the Continent. Hence drum tanning with powdered extracts does prove to be especially advantageous.

(c) Most of the tanners cannot afford to use costly chemicals for pretanning/pretreatments, etc., in view of the high cost of production that such an use entails.

Besides, conditions in India do not favour introduction of any revolutionary method of rapid tanning, involving, automation, rigid control of the entire tanning system and the use of costly and imported auxiliaries.

Taking into consideration all the above aspects, two processes have been formulated after many trials and the experimental details are given in the next page.

Experimental

3.6.1 Four pit system of tanning

Raw material: Wet salted buffalo hides medium - heavy range

Soaking: For 4 hours in plain water

Slaked lime:	10 per cent	Used lime liquor 200 percent
Sodium sulphide:	1 per cent	
Fresh water:	200 per cent	

handled twice a day - limed for 3 days.

4th day: Unhaired and relimed as follows for 3 days

Slaked lime:	8 per cent
Caustic soda:	0.5 per cent
Water:	400 per cent

7th day: Fleshed and noted the weight. Delimed overnight in a pit with

Ammonium sulphate:	2.5 per cent
Water:	150 per cent

8th day: After complete deliming, scudding and washing, put in suspender of 15°Bk made with wattle, myrab blend 2:1 (pH 4.2)

9th day: Put in 30°Bk liquor in suspender pH 4.1

10th day: Put in 60°Bk liquor in suspender pH 4.0 - 3.9

11th day: Put in 90°Bk liquor in suspender pH 3.9 - 3.8

(pH in the first pit was adjusted with dilute H_2SO_4. In the other stronger liquors, dilute formic acid was used for pH adjustment).

12th - 14th day: Drum tanned in 100°Bk liquor for a total duration of 16 hours (pH 3.8 - 3.75)

14th day: Taken out from the drum and put in pile

15th day: Washed and bleached with

Sodium bisulphite:	0.5 per cent
Oxalic acid:	0.25 per cent

Washed for 15 minutes and beamed and put in myrobalan liquor at 30°Bk.

Handled twice during the day.

16th day: Taken out, washed, beamed and stuffed with

+Urea:	0.5 per cent
T.R.O.	1.5 per cent
Raw pungam oil:	2.0 per cent

The drum was run for 20 minutes. Then 1 per cent formaldehyde was added and drum run for 1½ hrs.

Added 0.15 per cent oxalic acid dissolved in 10 times its weight of water. Drum run for 15 minutes. The leathers were taken out and hooked.

17th and 18th day: Set and allowed to dry.
19th day: Seasoned and rolled.

The Bk strength of the yard liquors after the tanning of one lot, were found to be 12°, 28°, 56° and 85°. The tail liquor on assessment was found to have a tannin content of 1.1 gms/100 cc. of the liquor. 1/5th of the tail liquor was drained out and 1/5th of the liquor from the next higher pit was added to bring the Bk back to about the original level. Similarly the second and third pits were strengthened and the fourth pit was also brought to the original strength. The run out liquor from the drum as well as required quantities of extract were used to strengthen the yard liquors.

Assessment

The leathers were of very pleasing, light colour with good temper and non-cracky. The yield was found to be 58 per cent.

The leathers were analysed for chemical and

+ For dark coloured leathers, the amounts of urea, formaldehyde and oxalic acid can be increased to 1 per cent, 2 per cent and 0.25 per cent respectively.

physical characteristics and the results are given below:

Moisture:	15.0 per cent
Oils and fats:	2.5 per cent
Water solubles	5.1 per cent
Insoluble ash	0.3 per cent
Hide substance	43.2 per cent
Fixed tannins: (By difference)	33.9 per cent
Degree of tannage:	78
pH of water solubles:	4.5
Differential figure	0.5

Physical testing:

	Loss of thickness in mm per		
	100 rev.	200 rev.	500 rev.
1. Abrasion resistance	1.07	1.55	2.51

	½ hr.	2Hr.	24 Hrs.
2. Water absorption Per cent	31.4	34.5	37.9

3. Apparent density: 0.93 gms/cc

It may be seen that the leathers conform to ISI specifications in all respects, other than Apparent Density, which should be at least 0.95 gms/cc. This actually enabled us to load the leather a little more, in our subsequent experiments.

Also, it was felt that the tannin content of 1.1 per cent in the tail liquor was a little too high. Hence it was decided to introduce one more pit of 10°Bk at the beginning and leathers were tanned with this five pit system.

3.6.2 Five pit system

The experimental methods were nearly the same as for the four pit system except for the following variations:

1st pit:	10°Bk	pH 4.2	(In the first two pits, the pH was adjusted with dil. sulphuric acid. In the stronger liquors dil. formic acid was used)
2nd pit:	20-22°Bk	pH 4.15 - 4.1	
3rd pit:	30-32°Bk	pH 4.10	
4th pit:	55°Bk	pH 4.0 - 3.9	
5th pit:	75°Bk	pH 3.9 - 3.8	

Drum tanning was done in 90°Bk liquor for 18 hours. (pH 3.8 - 3.75)

In stuffing, in addition to the recipe given in the previous process, 1 per cent epsom salt and 2 per cent glucose were also incorporated.

The tanning period was one day more than in the case of four pit system, i.e. from soaking to rolling it took 20 days time. The tannin content in the tail pit was found to be about 0.8 per cent.

In general appearance, feel, etc., the leathers were equally good as compared to the leathers from the four pit system. The leathers on analysis were found to conform to ISI specifications. The data are given below:

Moisture:	14.0 per cent
Oils and fats:	2.6 per cent
Water solubles:	8.6 per cent
Insoluble ash:	0.66 per cent
Hide substance:	44.64 per cent
Fixed tannins (by difference)	29.50 per cent
Degree of tannage:	66
pH of water solubles:	4.0
Differential number:	0.6
Apparent density:	0.949 gm/cc.

Physical testing

	Loss of thickness in mm per		
	100 rev.	200 rev.	500 rev.
Abrasion resistance	0.60	1.12	2.25
	½ hr.	2 Hrs.	24 Hrs.
Water absorption per cent	38.5	40.0	43.8

General conclusions

The four pit and five pit systems described above, provide excellent tanning methods for different types of commercial tanning particularly suited to India. These processes are easy, extremely economical and involve minimum chemical control, labour, automation, etc. The process may not be very rapid, but nevertheless they are quick compared to conventional sole leather tanning. They can be made still quicker by adopting a quick liming method, as described in Chapter 4 in this final report.

3.7 Studies on rapid tanning using pickling and subsequent depickling process

The method of pickling and depickling has been tried by several workers in the past for enhancing the quickness of tannage in sole leather manufacture. In the South African methods for rapid tanning, acid salt pickle is used in the Osmotan process, while a calgon-acid pickle is used in the Liritan process. In another experiment[23] J.K.De has tried rapid extract tannage of sole leather using a light salt and acid pickle, on limed pelt.

Light pickling and subsequent depickling with hypo is often practised in EI tanning where the tanners have found that the treatment improved the colour of

the leather. In our experiments here, it was attempted to study the effect of pickling and depickling of delimed hides, on the speed of penetration during vegetable tanning.

Pickling and depickling may probably facilitate more opening up of the fibres and fibrils and may even increase the reactivity of the active groups of collagen by making them more accessible to tans.

From our earlier studies as well as from the work of previous workers the importance of bringing the pelt to its isoelectric point prior to accelerated vegetable tanning is well established. Hence in this series of experiments the pelt pieces after light pickling and depickling were brought to as near the isoelectric points as possible.

Experimental

A wet salted buffalo hide was soaked, limed and delimed as for usual sole leather tanning. Then pieces of dimensions 8 inches x 8 inches were cut off from the butt portion. After thorough washing, the pieces were given a light pickling with 5 per cent NaCl and 0.5 per cent H_2SO_4 for about 6 hours in a glass trough. Then the pieces were taken for depickling.

For depickling the following salts were used individually.

(1) Sodium sulphite (2) sodium thiosulphate, (3) sodium acetate (4) sodium citrate and (5) borax. 5 per cent of these salts were dissolved in 100 per cent water (all on pelt weight) and kept in a separate trough and one piece each was put in these troughs for depickling. After 12 hours the pH values of the depickling baths were adjusted to about 4.5 - 4.8, with the addition of small amounts of dilute H_2SO_4 and the system was allowed to come to an equilibrium. Frequent handling was given to equate the pH inside and outside the pelt.

The pieces were next taken for vegetable tanning. They were placed straight in wattle liquor of 50°Bk. A control was carried out using a conventionally delimed piece without any modification. The rate of penetration was observed each day and recorded as shown below:

Table 9

Depickling agent used

	Na_2SO_3	$Na_2S_2O_3$	CH_3COONa	Borax	Sod.cit.	Control
Penetration in per cent						
In 48 hrs.	60	70	70	65	75	55
In 3 days	70	80	80	75	85	65
In 4 days	85	90	90	90	Full	75
In 5 days	Full	Full	Full	Full	Full	85
In 6 days	-	-	-	-	-	95
In 7 days	-	-	-	-	-	Full

From the observation, it may be seen that the operation of pickling and depickling helps to quicken the penetration in all the cases. After tanning, the leathers were assessed for their colour, feel, etc. and it was found in the case where sodium citrate was used for depickling, that the colour of the leather was extremely good. The leather had also a good temper, compactness and a smooth grain. Next best was the one in which sodium sulphite was employed as the depickling agent. Sodium thiosulphate, sodium acetate and borax gave quicker penetration no doubt, but the tannage as a whole was not comparable to the other tannages.

3.8 Use of lyotropic salts

It has been found that small quantities of calcium chloride or magnesium chloride in the common salt used

for preserving and curing, on prolonged storing lead to losses, in protein by degradation, probably through the association of $CaCl_2$ in the molecular form with the peptide bonds, an effect due to the concentrated solutions of chlorides present in the cured skins. During the soaking operation, lyotropic salts are useful for better wetting and hydration of skins. While liming, the calcium ions open up crosslinks of the hydrogen bond type, as a result of electrostatic intervention with the weakly polar peptide groups. In the washing and deliming of the limed skin, the choice of deliming agent is very important, since the accumulation of the deliming agents in the interstices of skin results in rather high concentrations of these compounds in the hide structure, in spite of only small percentages being employed.

The lyotropic effect is generally most pronounced in neutral solutions in which the specific effects of the ions or molecules do not have to compete with the powerful hydrogen and hydroxyl ions.

It has been reported by Gustavson[30] that in a molar solution of $CaCl_2$ the loss in hide substance is about 32 per cent while in salts like sodium sulphate, hypo and $MgSO_4$ the loss is only between 1-2 per cent. The order of increasing peptisation for cations is

Ca Sr Ba Mg Na,K. For anions is the order CNS I Br Cl SO_4, S_2O_3

The action of urea on collagen is in many respects similar to that of neutral salts.

In our experiments here, the object was to find out the effect of lyotropic salts on the penetration and fixation of tannins. The salts used were sodium chloride, sodium sulphate, sodium thiosulphate, potassium iodide, urea, calcium chloride and barium chloride.

3.9 A new approach for the manufacture of vegetable tanned leather

In India, heavy leathers are generally made with the blends of myrab (Terminalia chebula) babul (Acacia arabica) and wattle (Acacia mollisima) or only with wattle and myrab. The present trend of sole leather manufacture in India is to use more and more of myrab in the blend, since this tanning material is more easily available and its price is also comparatively low. These blends take about 2-3 months for the completion of heavy leather tannage. Considerable amount of sludge in the yard liquor is found to be deposited in course of tannage. Our studies showed[24] that the use of increased amount of myrab in the blend led to retarded penetration as was evident from non-uniform coloration of the cut section of the tanned piece. The slow penetration of the blend liquor might be due to the following reasons:

(a) When condensed tannins come into contact with acidic hydrolysable tannins, there is every possibility of the former getting polymerised, resulting in retarded penetration. This polymerisation of the condensed tan molecules depends on the relative amount of the hydrolysable tannins present in the blend.

(b) The myrab tans and nontans in the blend may undergo further hydrolysis forming bloom (sludge) in the tan liquor, and this may hinder the penetration of the blended liquor through the pelt.

(c) The myrab tan molecules being negatively charged[25] may have some affinity for the condensed tan molecules and when these are mixed together the resultant complex may have a slower rate of penetration.

Numerous references are available in the relevant literature in regarding heavy leather tannage using condensed tan materials like wattle and quebracho.

However, very few seem to have worked with the blend of hydrolysable and condensed tan materials. Presumably such blends did not lead to any significant advantage in quick tannage.

Benskin and Cheshire showed (as was also confirmed by our recent findings[26]) that the penetration of the tan liquor through the pelt was considerably increased when the pelt was brought to the isoelectric region.

Since increase in the proportion of myrab infusion in the blended tan liquor led to retarded penetration and more sludge formation, it was thought worthwhile to treat the pelt individually with these two types of tan materials in separate baths. This was expected to give us some idea about the efficiency of such a treatment vis-a-vis the conventional practice in respect of the quality of the leather produced and the amount of tannins consumed for the same.

Experimental

Preparation of tan liquors

(a) Myrab liquor:- Myrab liquor was prepared by two consecutive extractions of crushed myrab nuts with water in the ratio 1:4. The combined liquor was made upto pH 5 using sodium sulphite and the strength was then finally adjusted to 25°Bk.

(b) Babul liquor:- Babul liquor was prepared in the usual way by extracting the crushed babul bark on the countercurrent principle. The liquor was also made upto 25°Bk.

(c) Mangrove liquor:- A liquor of 25°Bk was made from spray dried mangrove extract from Andaman mangrove bark (Rhizophora mucronata).

(d) Wattle liquor:- A solution of 25°Bk was made using commercial wattle extract (Acacia mollissima) of known strength.

(e) Blend of wattle and myrab:- Required volume of 25°Bk. Wattle liquor was mixed with known volume of 25°Bk myrab liquor (freshly leached) so as to make a blend of 2:1 respectively.

(f) Blend of babul and myrab:- Required volumes of babul and myrab leach liquor (25°Bk) were mixed in the ratio of 2:1 respectively.

Tanning procedure

A wet salted buffalo hide was soaked, limed and delimed in the usual way. The butt portion (5 mm thick) was then taken and cut into 8 pieces each measuring 15 cm x 10 cm. Four pieces were then put in myrab liquor and the pelt/liquor ratio was adjusted to 1:15. They were handled twice a day and examined each day for the extent of penetration. After 4 days when the myrab treated pieces were fully struck through, three of these pieces were washed and put separately in wattle, babul and mangrove liquors, keeping the pelt/liquor ratio at 1:15. The 4th piece was kept in the same myrab liquor for five more days.

In another series, 3 pieces of delimed pelt were put separately in wattle, babul and mangrove liquor keeping the pelt/liquor ratio same as before. After the completion of penetration the pieces were kept in the liquor for 5 more days.

In the first series i.e., with myrab pretreated pieces, wattle penetrated in 3 days whereas both babul and mangrove took 9 days to penetrate. All the pieces were kept in the respective liquors for 5 more days following complete penetration. In the second series wattle penetrated in 6 days, babul in 11 days and in the case of mangrove, penetration was not complete even after 40 days.

At the end of the stipulated period all the pieces were taken out and the adhering liquor was

wiped off with moistened cotton wool. The pieces were kept in the dark for drying and then analysed for their chemical and physical properties. The residual liquors were also analysed for tan/nontan content. The results are given in the tables.

Discussion of results

From the results it was observed that in pieces pretreated with myrab the subsequent penetration of condensed tan materials needed much less time than in those treated straightaway with condensed tan materials only. Mangrove liquor known for its poor diffusion capacity through the pelt[27] penetrated through the myrab pretreated piece very quickly (9 days). In contrast, the original liquor failed to penetrate through the pelt even after 40 days. Likewise, wattle and babul liquors penetrated through the myrab pretreated pieces with comparative ease (in 3 and 9 days respectively) although these improvements were less marked than it was in mangrove. The penetration of the blended liquors took more time than the corresponding original condensed tan liquors.

The experiment thus showed that pretanning with myrab at pH 5 helped the penetration of condensed tan materials considerably. Presumably myrab containing more of phenolic nontans[28] penetrate through the pelt with sufficient ease and this helps the opening up of fibres and fibrils. When the myrab pretreated pieces are put in condensed tan liquors containing tannins of varying particle size some of these tan particles easily push themselves through the already opened up network of fibres and fibrils and get lodged there, displacing perhaps a part of myrab nontans already present there.

As regards degree of tannage it was observed that the leather pretreated with myrab followed by treatment with condensed tan materials showed a higher

degree of tannage than the one tanned without such pretreatment. The degree of tannage of the leather tanned with myrab was found to be the lowest followed by the leather tanned with the blends. Exception was observed in the case of the leather tanned with original mangrove liquor, in which case even though penetration was not complete over a period of 40 days, the degree of tannage nevertheless was found to be higher than the one pretreated with myrab and subsequently treated with mangrove. This is presumably due to the fact that in course of the contact time of 40 days a good amount of mangrove tannins got highly polymerised and got themselves fixed up on the surface of the pelt thereby giving a higher degree of tannage.

When the pelts are pretreated with myrab infusion, the myrab tannins are probably for the most part fixed by nonionic protein groups, while the sorbed matter apparently is held chiefly by the cationic protein groups without cross-linking[29]. But when the myrab pretreated pieces are put in condensed tan molecules, most of the sorbed matter is likely to be replaced by the higher mol.wt. condensed tan aggregates giving rise to higher degree of tannage. In the case of the leathers tanned with blended liquors, the degree of tannage was found to be very low. Presumably, the blend prevented the quicker penetration of the tan molecules through the pelts and consequently yielded a low degree of tannage.

The final weight yield was higher in case of all the myrab pretreated pelts as compared to those treated with condensed tan materials alone. The pieces tanned with the blends showed low yield. The myrab pretreated piece tanned with wattle showed about 6 per cent more yield than the one tanned with wattle only. Similarly, myrab pretreated piece tanned with babul showed 10 per cent more yield in comparison to that tanned with babul only. Myrab pretreated piece tanned with mangrove

showed slightly more yield than the mangrove tanned piece, which was of course left in the mangrove liquor for wuite a long time. The significant improvement in yield brought about by the myrab pretreatment might be due to the weight giving property of myrab. Since penetration and fixation were poor in the case of leathers tanned with the blends, the resultant yield was also poor.

The leathers pretreated with myrab followed by tannage with condensed tan materials showed almost the same Ts as those of the pieces tanned with the blends but a slightly lower value than those tanned with condensed tan materials only, myrab tanned piece as usual showed the lowest Ts. The higher Ts of the leather is generally ascribed to the strengthening of the existing cross links and the formation of new cross-links between the polypeptide chains. According to Gustavson[29] myrab tannin is probably for the most part fixed by the nonionic protein groups, while the sorbed matter is apparently held chiefly by the cationic protein groups without cross linking. When these myrab treated pieces were tanned with condensed tan materials, the sorbed portion of the extract is presumably replaced by the condensed tan materials, which are known to be powerful cross linking agents. Probabaly the condensed tan molecules themselves form new cross links and strengthen the existing cross-links of collagen thereby raising the Ts of the leather.

The water absorption capacity of all the pieces pretreated with myrab showed least value followed by that of the leathers tanned with the blended liquors. The leathers tanned only with myrab, babul and wattle showed the highest and almost the same water absorption after 24 hours. Mangrove tanned piece showed minimum water absorption. This is presumably due to the fact that mangrove tanned piece was tanned for 40 days and full penetration of the liquor through the pelt was not

effected. Once dried, the mangrove tannin is known to be less soluble in water. The water absorption capacity of all the pieces was found to be more than what is usual for sole leather. This is expected since the pieces were not heavily tanned or oiled and rolled.

The abrasion resistance of all the pieces tanned with myrab followed by condensed tan molecules showed the maximum value. This was followed by the leathers tanned with the blend and myrab only. The leathers tanned with the condensed tan liquors showed the least resistance to abrasion. This may mean that even though myrab tan molecules are not efficient cross linking agents, they do impart a good resistance to abrasion to the treated leather. Presumably, considerable bloom formation inside the leather contributed to the increased resistance to abrasion.

The colour of all the pieces pretreated with myrab followed by condensed tan liquor was the best of the series, that of the leathers tanned with the blends coming second. The leathers tanned with condensed tan liquors only, was the darkest in colour.

From the analysis of the spent tan liquors it was observed that the liquors used for tanning the myrab pretreated pelts contained more of tans than those in which pelts were tanned without pretreatment. Wattle tan liquor used for tanning myrab pretreated pelt contained about 40 per cent more tannin in the spent liquor as compared to the corresponding residual liquor in respect of the pelts not subjected to any pretreatment. Babul and mangrove liquors used for myrab pretreated pelts contained about double the quantity of tannin in the spent liquors in each case as compared to the one for leathers tanned without any pretreatment. From the analytical figures of the spent liquors it is evident that the pelt used in condensed tan liquors alone had taken

up about 60 per cent of tannin from the wattle tan liquor whereas the myrab pretreated one absorbed only about 30 per cent. This showed that if the pelts are pretreated with myrab about 30 per cent less of wattle tannin is needed to achieve the desired properties of the leather. The pelts tanned with babul and mangrove liquors as such absorbed about 77 per cent and 82 per cent of tannin respectively in contrast to the myrab pretreated pelts absorbing about 37 per cent and 62 per cent tannins i.e. about 40 per cent and 28 per cent less than the corresponding figures in the former series.

The experiment thus showed that if the delimed pelts are first treated with myrab around pH 5 for a few days till the penetration is completed and are then finally tanned in condensed tan liquors, a considerable saving of condensed tan extract may be effected. Penetration time of the condensed tan infusions through the myrab pretreated pelt is also considerably reduced, even though the overall tanning time for wattle and babul is slightly increased. In the case of mangrove however, the total tanning period is considerably reduced. Moreover, myrab pretreatment at the same time ensures most of the desirable properties in the final leather in respect of yield, degree of tannage, water absorption, abrasion resistance and colour as attained with other series in comparison. Since the myrab pretreatment is carried out around pH 5 the sludge formation in the liquor is also reduced to the minimum.

It therefore seems as though the same technique may be advantageously followed for the manufacture of sole leather (both pit and bag tanned), E.I. kips and skins, etc., with considerable economy in the use of condensed tannins.

ANALYSIS OF THE TAN LIQUORS

	Myrab		Wattle			Babul		
	Initial	After tanning the delimed pelts	Initial	After tanning the delimed pelts	After tanning the myrab pretreated pelts	Initial	After tanning the delimed pelts	After tanning the myrab pretreated pelts
Total solubles gms./litre	67	43	69	31	42	57	23	37
Tans (gms./litre)	34	10	47	23	29	30	7	19
Nontans (gms./litre)	33	33	22	8	13	27	16	18
^{o}Bk	25	20	25	12	15	25	11	16

ANALYSIS OF THE TAN LIQUORS

	Mangrove			Babul + Myrab(2:1)		Wattle + Myrab(2:1)	
	Initial	After tanning the delimed pelts	After tanning the myrab pretreated pelts	Initial	After tanning the delimed pelts	Initial	After tanning the delimed pelts
Total solubles gms./litre	67	20	29	55	22	68	25
Tans(gms./litre)	34	14	13	37	8	41	17.5
Nontans (gms./litre)	33	6	16	18	14	27	7.5
^{o}Bk	25	14	15	25	12	25	12

Chemical properties of the leathers
(Chemical analysis on 14 per cent moisture basis)

Sl. No.	Leather tanned with	Insoluble ash (per cent)	Water solubles (per cent)	Hide substance (per cent)	Fixed tan (per cent)	Degree of tannage	Yield (per cent) on delimed pelt wt)	Penetration (days)
1.	Myrab	Negligible	9.05	57.49	21.46	37.30	50	4
2.	Babul	-do-	10.12	51.14	26.74	52.30	55.35	11
3.	Wattle	-do-	13.59	46.69	27.70	59.30	62.15	6
4.	Mangrove	-do-	6.5	45.54	36.00	80.00	61.00	10 per cent remains even after 40 days
5.	Myrab followed by babul	-do-	10.77	48.87	28.30	58.70	65.27	9
6.	Myrab followed by wattle	-do-	14.42	44.50	29.01	65.40	68.65	3
7.	Myrab followed by mangrove	-do-	7.7	50.95	29.31	58.00	64.00	9
8.	Blend of myrab and babul	-do-	8.4	51.8	25.80	49.8	55.00	15
9.	Blend of myrab and wattle	-do-	9.4	50.6	26.0	51.4	60.0	8

Table 12 Physical properties of the leathers

Sl. No.	Leather tanned with	Abrasion resistance (loss of thickness in mm for 500 revolutions)	Water absorption		Ts (°C)
			2 hours	24 hours	
1.	Myrab	3.75	92.8	106.7	65
2.	Babul	4.45	106.5	112.8	82
3.	Wattle	4.69	92.5	100.3	85
4.	Mangrove	2.36	75.3	87.9	82
5.	Myrab followed by babul	2.79	78.3	84.4	80
6.	Myrab followed by wattle	2.92	71.1	76.2	82
7.	Myrab followed by mangrove	3.55	83.0	89.3	80
8.	Blend of myrab and babul	3.8	86.5	92.4	81
9.	Blend of myrab and wattle	4.0	75.2	82.3	83

4. MISCELLANEOUS STUDIES

4.1 Investigation on the rate of uptake of vegetable tannins with respect to time and concentration

The object of this work was to study the variation in the rate of penetration, when pelt pieces are treated with vegetable tan liquors of different tan concentrations.

Mimosa liquor was prepared and adjusted to different barkometer strength of 10^{o}, 20^{o}, 30^{o}, 40^{o}, 50^{o}, 60^{o}, 70^{o}, 80^{o}, 90^{o} and 100^{o}Bk. Delimed pelt pieces of approximately 25 grams each was put in these liquors and the pelt/liquor ratio was maintained at 1:10 in all the cases. The rate of penetration was observed each day and the results were recorded as follows:

Table 13. Penetration in per cent each day

Strength of liquors	Ist day	2nd day	3rd day	4th day	5th day	6th day	7th day	8th day	9th day	10th day	11th day
10^{o}Bk	20	30	40	50	55	60	65	70	80	90	95
20^{o}Bk	30	40	50	55	60	70	70	80	95	Full	-
30^{o}Bk	35	50	60	65	70	75	85	95	Full	-	-
40^{o}Bk	40	55	60	65	65	75	85	95	Full	-	-
50^{o}Bk	45	60	70	75	80	90	Full	-	-	-	-
60^{o}Bk	45	65	70	75	85	95	Full	-	-	-	-
70^{o}Bk	50	65	75	80	90	Full	-	-	-	-	-
80^{o}Bk	50	70	80	90	Full	-	-	-	-	-	-
90^{o}Bk	50	65	75	80	85	95	-	-	-	-	-
100^{o}Bk	45	60	75	80	85	95	98	Full	-	-	-

From the data it may be very clearly seen that the concentration has got a very prominent part to play in the rate of penetration. While a liquor of low concentration(10^{o}Bk) takes about 12 days to penetrate, liquors from 50^{o}Bk and above take less

than 7 days to penetrate through completely.

As from the above observations, an 80°Bk liquor seems to give the quickest penetration, but a cut edge of the tanned piece does not show uniform fixation of tans inside the pelt. So also in the case of still stronger liquors the tanning tended to take place more in the grain, less in the flesh and least in the middle. So obviously it is not advisable to commence tanning in liquors of concentrations greater than 50°Bk or the pelt should be given suitable pretreatment.

The same experiments were repeated after the pelt pieces were treated with a buffer of sodium citrate and citric acid to pH 4.8. It was observed that the rate of penetration improved in all the cases especially in the liquors of lower concentrations.

In certain processes of sole leather manufacture, the tanning may commence with a liquor strength of 50°Bk and above. Also it may not be possible to use a rundown system and hence the liquors once used may have to be reused again and again, after bringing those liquors to their original strength by adding concentrated extracts. But these reused liquors are apt to slow down the speed of the tannage. In order to study this, certain experiments were conducted to find out the variation of the speed of penetration with reused liquors.

Wattle liquor of 30°, 40°, 50°, 60°, 70° Bk strength were prepared and pelt pieces were put in these liquors, keeping the pelt liquor ratio 1:20. The rate of penetration was observed each day. Penetration was over in 6 days for liquors of 50°Bk and above while those of 40°Bk took 8 days and 30°Bk 9 days.

After the first batch of tannage, the Bk strength of all the liquors was brought to their original level

by the addition of small amounts of very concentrated wattle liquor and a fresh lot of pelt was put in the liquors.

It was observed that the penetration was reduced in all the cases. In the higher concentrations the decrease in the rate of penetration was not much but in the concentrations below 50°Bk, the penetration was much reduced.

Ropiness was noticeable in all the liquors and more so in weaker liquors. In the third batch of tanning, penetration was found to be still reduced.

4.2 Study on the viscosity of certain indigenous vegetable tanning infusions

While commenting on some of the investigations on the tanning velocity in the rapid tanning of heavy leathers[7], Woollenberg has emphasises the need to keep the viscosities of the tanning infusions as low as possible. While in countries abroad wattle is the widely accepted material for rapid tanning, in India the tanning is mostly done with blended liquors using babul, myrab, mangrove, etc. It was thought worthwhile to study the viscosities of different tan materials individually and in their blends with another hydrolysable tan material like myrab along with the effect of ageing on such viscosities.

4.2.1 Variation in viscosity due to blending with myrobalan

Approximately 25°Bk infusions of the following were prepared.

I	Wattle	
II	Babul	
III	Mangrove	
IV	Myrobalan	
V	Wattle myrob blend	1:1
VI	-do-	1:2
VII	-do-	1:3

VIII	Wattle myrob blend	1:4
IX	Babul myrob blend	1:1
X	-do-	1:2
XI	-do-	1:3
XII	-do-	1:4
XIII	Mangrove myrab blend	1:1
XIV	-do-	1:2
DV	-do-	1:4
XVI	-do-	1:4

The liquors were first centrifuged and then filtered through a Whatman No.11 filter paper to ensure absolute clarity of the solutions. Then all the liquors were standardised to a constant sp. gravity of 1.020 by means of a hydrostatic balance. Subsequently viscosity measurements were made using a standard 'Ostwald' Viscometer. The readings are tabulated below:

Table 14

Liquor	Time taken for flow		Viscosity
	Minutes	Seconds	Dynes/sq.cm.
I Wattle	2	5	11.0
II Babul	1	55	9.5
III Myrobalan	1	50	9.1
IV Mangrove	2	15	13.5
V Wattle Myrob 1:1	2	0	10.06
VI -do- 1:2	1	59	9.98
VII -do- 1:3	1	57.4	9.88
VIII -do- 1:4	1	56.8	9.80
IX Babul Myrob 1:1	1	57.0	9.80
X -do- 1:2	1	56.0	9.61
XI -do- 1:3	1	54.8	9.52
XII -do- 1:4	1	53.1	9.33

Table 14 (Contd.)

Liquor			Time taken for flow		Viscosity Dynes/sq.cm.
			Minutes	Seconds	
XIII	Mangrove Myrob	1:1	2	10.2	13.0
XIV	-do-	1:2	2	8.0	12.1
XV	-do-	1:3	2	5.0	11.0
XVI	-do-	1:4	2	4.1	10.8
XVII	Distilled water		1	38.5	8.1

From the results, it was observed that the viscosity of infusions decrease in the following order, viz., mangrove, wattle, babul and myrobalan. Also it was found that blending with myrobalan induces progressive lowering of viscosity.

4.2.2 Variation in viscosity due to ageing

20°Bk solutions of babul, wattle, myrobalan and mangroves were prepared. These solutions were centrifuged and filtered and their sp.gr.values were measured accurately by means of a hydrostatic balance. Then the viscosities were determined by means of a standard Ostwald's Voscometer accurately noting the time of flow with a stop watch. For comparison, as well as for calculating the coefficient of viscosity, distilled water was run through the viscometer.

After the determination of viscosity, the liquors were aged for 10 days. Then they were centrifuged and filtered to remove the sludge and other insolubles. Their sp.gr. values were measured again and their viscosities determined as detailed earlier. The results are tabulated in the next page.

Liquor	Sp.g.	Time in seconds	Viscosity dynes/sq. cm.
1.Myrob liquor(fresh)	1.016	16	8.51
2.Myrob liquor (aged)	1.002	15.8	8.52
3.Babul liquor(fresh)	1.016	16	8.51
4.Babul liquor(aged)	1.012	16.3	8.60
5.Wattle liquor(fresh)	1.0158	17.2	9.14
6.Wattle liquor(aged)	1.020	18.0	9.40
7.Mangrove (fresh)	1.016	19.0	10.16
8.Mangrove (aged)	1.020	25	14.20
9.Distilled water	0.9970	15	8.10

From the results given above, it may be seen that ageing tends to increase the viscosities of the tan liquors generally. In the cases of babul and myrobalan liquors where there was more of sludge deposition and consequent lowering in density, this was not very apparent, but in wattle and mangrove liquors, the increase in viscosities in the case of aged infusions, were clearly perceptible.

4.3 Studies on the penetration of tan infusions through pelt and gelatine gel

4.3.1. Back-ground information

In 1911, Hoppenstedt[34] studied the diffusion of tannins of various tannin infusions into a layer of gelatine and found out that the order of diffusion was roughly in the order of decreasing astringency. Mezey[35] studied the rate at which tan liquors penetrated into calf skins. Diffusionwas measured by sectioning the leather with a microtome and staining the sections with $K_2Cr_2O_7$ and measuring the depth of penetration by means of a micrometer under a microscope. The bichromate on staining produced a brownish black colour on the tanned portion. The slides showed that the rapidity of diffusion cannot be correlated to astringency since quebracho and chestnut penetrated more rapidly

than sumac. Mezey maintains that the general opinion that the so called astringent tannins penetrate slowly is correct only when referred to concentrated solutions and that the diffusing power of these as such is not necessarily slow.

Stather[36] has also studied the diffusion of various tannins into the pelt. It has been found that the tannin diffusion from dilute solutions may be expressed by the formula $E = K\sqrt{T}$, where E is equal to the diffusion and is proportional to the square root of the time of tanning and where K is the Diffusion Constant. This constant has approximately the same value for 5 to 24 hours, but tends to increase with longer time. Taking the diffusion constant of gambier as 100, the various other tanning materials have been classified into four groups as follows:-

I	Low rate	Pine bark 28
II	Medium rate	Mangrove 46
		Myrobalan 50
		Sumac 52
III	Fairly rapid	Ordinary quebracho 63
		Chestnut 66
		Oakwood 69
		Algarobilla 74
IV	Rapid	Mimosa 78
		Sulphited quebracho 83
		Valonia 89
		Gambier 100

Further, there seemed to be no relation between penetration and astringency. The various materials were also brought to pH 4.0 and their diffusion rates determined, when they all showed essentially the same rate as above.

J.A.Wilson[37], who studied the rate of penetration (into hides of equal thickness) of various vegetable tanning materials, has placed Mimosa as the quickest

penetrating material. He gave the following figures as the time in days taken for complete penetration.

1) Mimosa	11 days
2) Chestnut	14 days
3) Cutch	16 days
4) Sulphited quebracho	18 days
5) Hemlock	19 days
6) Valonia	20 days
7) Oak	30 days
8) Myrobalan	33 days

Concerning the behaviour of different vegetable tanning materials in rapid tannage, Herfeld[38] and Hartëwig have made the following observations. With mimosa extract, complete penetration of the hide was achieved during the suspender pit process. Similarly with quebracho extract almost complete penetration was achieved at the end of the suspender pits, when the less acid liquors were used. It was undoubtedly possible to accelerate penetration by employing stronger sulphiting. With chestnut and oakwood extract, at the end of the suspender pits, the cross section of the hides showed a clear zone of approximately 20 - 25 per cent. Hence the speed of tanning declines in the following order - Mimosa, quebracho, chestnut and oakwood extract.

Scope of the present investigation

In our experiments, it was attempted to study the penetrating power of indigenous tanning materials as compared to that of wattle. Also the penetrating capacity of the different tanning infusions through different kinds of pelts viz: goat skin, sheep skin, cow hide and buffalo hide and buffalo grain split in the delimed state and also after subjecting them to various pretreatment, was determined in order to obtain relevant information regarding the rapid tanning of hides and skins. In another set of experiment it was aimed to determine the speed of

penetration of various tan liquors through a column of solidified gelatine. Also in some of these experiments certain conditions, like the pH of the liquor as well as the pH of the gel were altered to observe the variation in the penetration rate under the varying conditions.

Designing and construction of the apparatus

The apparatus consists of two cylinderical tube of 3 inches diameter. The connecting ends of both the tubes are flattened and ground. The pelt is cut into a circular form and is placed in between the fl ends of the tubes and held very tight by means of screw clips/and washers. The liquor under study is poured into the upper tube, where it comes into contact with the grain side of the pelt. The time taken for the tannin infusion to penetrate through the thickness of the hide is measured by visual observation.

Experimental

4.3.2 Penetration through gelatine columns

Pure gelatine flakes were soaked in ten times their weight of water and after allowing them to swell, the mixture was gently warmed on a water bath till the gelatine was completely dissolved. The solution was cooled to about room temperature and was divided into three parts. The pH values of two of the three fractions were adjusted to 2.0 and 6.0 respectively, leaving the third fraction at its natural pH of 4.3. Then minute quantities of ferrous ammonium sulphate solution was added to each of this fraction and the solutions were poured into different measuring cylinders (capacity 10 ml) to a level of 5 ml. and left in the refrigerator for the gelatine to set.

Tannin infusions of wattle, mangrove, babul and myrobalans were prepared under controlled conditions and adjusted to 20°Bk. 5 ml portions of these filtered

infusions were gently added to the gelatine columns in the measuring cylinders. The penetration of the liquor through the gelatine columns could be observed by the appearance of the blue colour formed by the interaction of tannins with ferrous ammonium sulphate. The depth of penetration was observed at intervals of 2 hours, 6 hours and 24 hours.

Similarly experiments were also conducted after varying the pH of the liquors on either side of their natural pH. The results are tabulated in Table No.16

4.3.3 Penetration through pelt pieces

Wet salted goat skin was soaked, limed, unhaired, relimed and fleshed as for E.I. tanning. After deliming and scudding, circular pieces of the required diameter were cut off from the butt portion. Similarly for cow hides and buffalo hides, soaking, liming and other pretanning operations were carried out as for usual vegetable tanning for kips in the former and for sole leather in the latter. After deliming and washing, circular portions were cut off from the butt portion.

Pelt pieces prepared as above were pressed firmly between folds of filter paper to remove the adhering water. Then each piece was mounted between the rounded edge of the two half cylinders in each of the apparatus and secured firm withwashers and screw clips as described earlier. Tannin infusions of wattle, myrob, mangrove and babul were prepared and adjusted to 20^{o}Bk. 50 ccs of these liquors were poured into the upper halves of the apparatuses. The time for penetrationof the tannins through the cross section of the pelt was observed in the following sequences (1) Appearance of the first coloured drop on the lower side of the pelt (2) appearance of the first drop giving a positive test with gelatine salt and (3) complete penetration through the pelt as evidenced from a cut edge of the pelt.

After the experiments were over the pieces were taken out and their shrinkage temperature determined.

In certain other experiments, pretreated pelts were used. For this, the delimed pelt was brought to isoelectric point with a buffer mixture of 0.1 N citric acid and 0.1 N sodium citrate. In another case, the pelt was pretreated with 1 per cent HCHO solution for 24 hours before mounting it on the apparatus. In another case the pelt was pickled and then lightly chromed before taking it for penetration studies.

The observations are recorded in Table No.17

Results and discussion

(a) Penetration through gelatine column

From the results it may be seen that babul stands first, regarding the speed of penetration followed by myrobalan, wattle and mangrove. In mangrove the penetration is very slow and in fact, it is not appreciable even after 4 days.

As regards to the effect of the variation of the pH values of the gel as well as that of the liquors, it was observed that uniformly the speed of penetration improved with the higher pH values in both the cases.

(b) Penetration through pretreated and untreated pelts

(1) Goat skins 1 (untreated)

It was found from the results that the speed of penetration decreases in the following order viz: wattle, babul, myrobalan and mangrove.

(2) Goat skins (Sodium citrate - citric acid buffer pretreatment to pH 4.8)

This buffer pretreatment increased the penetration rate in all the cases and more markedly in the case of babul and myrobalan.

(3) HCHO pretreatment

The time taken for complete penetration was reduced in all the cases.

(4) HCHO + HCOOH Pretreatment

Almost the same trend observed in the case of HCHO pretreatment is observed here. However in case of wattle, it is found that the rate of penetration is still enhanced.

(5) Chrome pretreatment

Chrome pretreatment seems to have an adverse effect on the rate of penetration, since in all the cases the penetration was found to be slower.

Cow hides

The results observed were more or less on the same line as in the case of goat skins. Regarding the experiments with pretreated pelts it is found that buffer treatment as well as HCHO and HCHO + HCOOH, improve the penetration rate fairly well especially in the case of mangrove.

Buffalo grain split

Here also it is found that the buffer treatment as well as HCHO + HCOOH treatment help considerably in reducing the penetration time.

As regards chrome pretreatment, it was observed that the penetration is retarded in all the cases.

4.3.4 Results in brief

It was observed that the increase in penetration of the tan liquor through gel columns was dependent on the pH of the tan liquor. Babul stands first in respect of penetration followed by myrobalan, wattle and mangrove. In mangrove, the penetration was very slow and in fact it was not appreciable even after 4 days. The penetration rate of liquors were not much affected by the increase in the pH of the gel.

When the pH of the liquor is high, the aggregation of the tan molecules is reduced with the

result, these can penetrate through the pelt more easily. Myrob which is a typically hydrolysable tannin is found to penetrate more rapidly when its pH is increased. But the rate of penetration of mangrove do not improve similarly. Presumably, mangroves containing more of aggregated molecules in addition to gummy matter cannot penetrate through the gel column even when the pH is very high.

From the result of the rate of penetration of the liquors through the untreated pelt, wattle was found to be the quickest followed by babul, myrobalan and mangrove.

The buffer pretreatment increases the penetration rate of the liquor through the untreated pelt, wattle was found to be the quickest followed by babul, myrobalan and mangrove.

The buffer pretreatment increases the penetration rate in all the cases and more markedly so in the case of babul and myrob. When the pelt is treated with HCHO, penetration is quicker in the case of myrob and babul.

Table 16 Penetration through gelatine column

Tanning material	pH gel	pH liquor	Penetration (in mm) 2 hrs.	6 hrs.	24 hrs
Myrobalan	2.0	2.0	3	9	14
		3.55	6	12	15
		6.00	7	14	9
	4.3	2.00	4	10	15
		3.55	5	12	15
		6.00	6	14	19
	6.0	2.00	3	10	16
		3.55	5	12	15
		6.00	5	13	17
Babul	2.0	3.50	6	10	19
		5.30	5	10	15
		6.00	7	11	18
	4.3	3.50	6	10	18
		5.30	7	12	22
		6.00	9	13	25
	6.0	3.50	7	11	25
		5.30	8	12	19
		6.00	9	13	20
Mangrove	2.0	3.50			
		4.90	NIL	NIL	NIL
		6.00			
	4.3	3.50			
		4.90	NIL	NIL	NIL
		6.00			
	6.0	3.50			2
		4.90	Trace	Trace	1
		6.00			2
Wattle	2.0	3.50	2	3	5
		4.90	1	3	5
		6.00	2	3	6
	4.3	3.50	2	4	9
		5.00	1	3	5
		6.00	3	5	10
	6.0	3.50	1	3	9
		5.00	1	3	5
		6.00	3	4	9

Table 17

Penetration through delimed skins and hides

Material	Tan liquor	Time for the appearance of first coloured drop.(mts)	Time for the appearance of first drop giving +ve test with gelatin-salt soln. (Hrs.mins)	Time for complete penetration (hrs. mins)	Ts ^{0}C
(1)	(2)	(3)	(4)	(5)	(6)
Delimed goat skin(1 mm thickness)	Myrab	15	2.0	2.50	68
	Wattle	30	1.15	3.00	84
	Babul	30	2.30	4.00	81
	Mangrove	30	3.00	7.00	82
Delimed goat skin pretreated with citrate - citric acid buffer	Myrob	15	1.30	2.30	68
	Wattle	30	1.15	2.45	85
	Babul	30	2.15	3.30	81
	Mangrove	30	2.50	5.00	83
Goat skin pretreated with HCHO	Myrob	15	1.30	2.00	71
	Wattle	30	1.15	2.30	88
	Babul	30	2.15	3.00	85
	Mangrove	45	2.45	5.00	88
Goat skin pretreated with HCHO + HCOOH	Myrob	15	1.30	2.00	71
	Wattle	30	1.30	2.30	88
	Babul	30	2.30	3.00	85
	Mangrove	35	2.45	5.00	88
Goat skin pretreated with chrome	Myrob	30	1.30	3.00	106
	Wattle	60	1.30	3.00	120
	Babul	30	2.30	3.30	106
	Mangrove	75	2.45	6.00	110
Delimed cow hide	Myrob	30	2.30	4.00	70
	Wattle	45	4.00	10.00	83
	Babul	1 hr.	4.00	10.00	82
	Mangrove	2 hrs. 30 mts.	10.00	30.00	82

Table 17 (Continued from previous page)

(1)	(2)	(3)	(4)	(5)	(6)
Cow hide treated with buffer	Myrob	30	2.15	3.30	71
	Wattle	35	3.00	5.00	84
	Babul	45	2.30	5.00	82
	Mangrove	2 hrs.	3.00	7.00	82
Cow hide pretreated with HCHO	Myrob	30	2.30	4.00	72
	Wattle	45	3.30	6.00	88
	Babul	45	2.45	5.00	87
	Mangrove	2 hrs.	3.15	8.00	86
Cow hide pretreated with HCHO + HCOOH	Myrob	30	2.30	4.00	71
	Wattle	45	3.30	5.30	85
	Babul	45	3.00	5.30	87
	Mangrove	1 hr. 30 mts.	3.00	7.00	88
Cow hide pretreated with chrome	Myrob	2 hrs.	3.00	4.30	105
	Wattle	5 hrs.	6.00	10.00	114
	Babul	3 hrs.	6.00	12.00	113
	Mangrove	6 hrs.	10.00	15.00	111
Delimed buff grain split 1mm(thick)	Myrob	30	4.00	6.00	70
	Wattle	1.15	5.00	8.00	86
	Babul	1.30	5.00	10.00	85
	Mangrove	3 hrs.	8.00	15.00	87

Table 17 (Contd.)

(1)	(2)	(3)	(4)	(5)	(6)
Buffer pre-treated buff grain split	Myrob	30 mts	2 hrs	4 hrs	71
	Wattle	1 hr.	1½ hrs	3 hrs	85
	Babul	2 hrs.	3 hrs	4 hrs	82
	Mangrove	2½ hrs	3½ hrs	6 hrs	85
HCHO treated	Myrob	20Mts	1 hr	2 hrs	77
	Wattle	1 hr	3½ hrs	4½ hrs	87
	Babul	40 mts	1½ hrs	3½ hrs	85
	Mangrove	3/4 hrs	2½ hrs	4 hrs	90
HCHO + HCOOH pretreated buff	Myrob	15 mts	1 hr.	2½ hrs	80
	Wattle	1½ hrs	3½ hrs	4½ hrs	89
	Babul	1 hr.	1½ hrs	2½ hrs	87
	Mangrove	1 1/4 hrs	2 hrs	2½ hrs	90
Chrome pre-treated	Myrob	2 hrs	4 hrs	10 hrs	108
	Wattle	3 hrs	5 hrs	12 hrs	114
	Babul	2½ hrs	6 hrs	15 hrs	111
	Mangrove	4 hrs	10 hrs	25 hrs.	115

4.4 Studies on the leaching systems of some indigenous vegetable tanning materials

Leaching of vegetable tanning materials is usually practised by Indian tanners by blending different tan materials (hydrolysable and condensed) together. In some parts of India, the blending of tanning materials is generally done only with babul and myrab and in some other parts the blending is practised with mangrove, babul and myrab or wattle, babul and myrab, etc. The blended liquors are prepared by counter-current technique in 8-10 days. But it is known that the solubility of hydrolysable tannins with water is much more than that of condensed tannins, as the former being ester type of tannins are less agglomerated and easily become soluble. The enhanced solubility is also due to more of hydroxyl groups in the hydrolysable tannins. But the condensed tannins which remain in highly aggregated form and having less of hydroxyl groups are slowly soluble in water. Recent work has shown that infusions of myrab[31] and babul[32] if exposed to atmosphere for about a week, about 40 per cent and 20 per cent of tannins respectively are precipitated out in the form of sludge. It has also been observed that the bark of typical condensed tannin like mangrove[33] on drying loses a considerable portion of its extractable tannins. If the bark is crushed properly the extraction of some of the condensed tannins becomes easier.

The present work is designed to study the merits and demerits of the present leaching system with a view to improving the same.

Experimental

Four different sets of experiments were conducted namely:

1. Individual leaching of different tanning materials namely myrab (*Terminalia chebula*), babul (*Acacia arabica*), Mangrove (*Ceriops roxburghiana*) and wattle (*Acacia mollisima*)

2. Blended leaching of babul and myrab and mangrove and myrab.

3. Individual leaching of myrab in 12 hours

4. Individual leaching of myrab, babul and mangrove and then blending.

1. Individual leaching of different tanning materials

Three different sets of experiment were conducted as follows:

(a) 100 gm. of different tanning materials namely myrab, babul, mangrove and wattle (all in dried condition) after crushing in almost powder form ($\frac{1}{2}$ inch mesh size) were soaked separately with 400 ml. of water (30°C) for 12 hours, after which the leached infusions were filtered. The volume of the filtrates of each was recorded and the same volume of water was again poured in the respective tanning materials and kept 12 hours more in the similar way. The leached infusions were again filtered. In this way the different tanning materials were extracted 4 more times. In the similar way, in another set of experiment the tanning materials were leached first 4 times with cold water (30°C) and last 2 leachings with boiling water (the water was only boiled and poured on the tanning materials).

(b) In another set of experiment the different tanning materials were taken in the similar way as are generally taken in some commercial tanneries+ i.e. without reducing the size of the tanning materials considerably. Other procedures are the same as before.

(c) In the third set of experiment, the crushed myrab and babul were leached separately with water at 10°C. The extraction procedure was the same as

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+1 inch x 1/4 inch in the case of babul, wattle and mangrove and in the case of myrobalan nuts, breaking them into two